

# Effect of Stearic Acid and Sodium Stearate on Cast Cornstarch Films

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**ABSTRACT:** Stearic acid and sodium stearate were used as lipids to form inclusion complexes with cornstarch through a cooking process, respectively. The complexing index and the surface tension of the cooked pastes were measured. The films of the pastes were formed by casting, paper-sizing, and paper-coating methods. X-ray diffraction and scanning electron microscopy were used to characterize the crystal and surface structures. Such properties of the complex films as the moisture absorption, friction coefficient, and tensile properties were tested. The results reveal that the two lipids could form an inclusion complex with amylose in the cornstarch more or less as a result of forming V-type crystals that restrained the crystallite size

of the B-type crystal in the starch film. The addition of lipids reduced the sensitivity of the complex films to environmental moisture, decreased the friction coefficient of the films, and visibly increased the smoothness of the surfaces of the films. When the lipids were added in the starch at a weight content of 1%, the elongation at break of the complex film increased and the strength decreased slightly, and above a 1% content of the lipids, the tensile properties of the starch film were greatly deteriorated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3782–3791, 2012

**Key words:** biopolymers; films; inclusion chemistry; polysaccharides

## INTRODUCTION

There are mainly two glucosidic macromolecules, linear amylose and branched amylopectin, in starch granules. It has come to light that amylose is a linear  $\alpha$ -glucan polymer with 99%  $\alpha$ -D-(1,4) linkages with a molecular weight of approximately  $1 \times 10^5$  to  $1 \times 10^6$ .<sup>1</sup> The stable conformation of amylose is a left-handed single-helix structure consisting of six D-glycosyl units per turn<sup>2</sup> with hydroxyl groups of glucosyl residues located on the outer surface of the helix so that the internal cavity becomes a hydrophobic tube,<sup>3</sup> known as a *V-type structure*.<sup>4</sup> Therefore, amylose shows a unique ability to form helical inclusion complexes with a variety of organic and inorganic ligands, such as iodine,<sup>5</sup> lipids,<sup>6</sup> alcohols,<sup>7</sup> and surfactants.<sup>8</sup> Several studies<sup>4,6,9–11</sup> have shown that an amylose–lipid complex forms in hot water and is easy to precipitate on cooling as a result of V-type crystallization. In the case of amylose–fatty acids, the driving force of the formation of the V-type inclu-

sion complex is hydrophobic interaction between the fatty tails and the internal cavity of the amylose single helix, and the thermal stability of the complexes increases with both the amylose chain length<sup>9</sup> and the lipid chain length.<sup>10</sup> When amylose chains were synthesized from monodisperse linear dextrin primers catalyzed by potato phosphorylase, monodisperse short chain amylose–lipid complexes can be formed in the presence of lipids.<sup>10,11</sup> In the course of amylose synthesis, there is a minimal amylose chain length necessary to accommodate the first molecule of the lipid ligand, and then, the amylose chain extension occurs together with subsequent complexation of the lipid until the complex becomes insoluble and precipitates.<sup>11</sup> It is well known that the polar carboxyl groups of fatty acids located outside the hydrophobic cavity of an amylose tube<sup>12,13</sup> and fatty acids are limited to two molecules in a helical segment length with their terminal methyl groups end-to-end.<sup>4,14</sup> On the basis of experimental observations of the precipitation of the complexes, Gelders et al.<sup>10</sup> proposed a lamellar amylose–lipid complex model with alternating amorphous and crystalline layers, consisting of rodlike or U-shaped complexes or their combination.

The properties and function of a starch-based material can be affected by the complex formation of its amylose with a ligand as a result of changes in the supramolecular structures. In this connection, more attention has been paid to the pasting behaviors of

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the starch–lipid system.<sup>3,4,7,15–18</sup> In some instances, an amylose–glycerol monostearate complex forms outside starch granules when the starch is gelatinized in the presence of glycerol monostearate in water; this decreases the granule swelling and amylose leaching.<sup>8</sup> On the contrary, as palmitic acid is added in starch suspensions, it decreases the gelatinization temperature of starches.<sup>16</sup> The gelatinization rate and viscosity of a starch suspension in the presence of lipids are greatly affected by the fatty acid chain length; this could be attributed to the mechanism in which amylose molecules with shorter chains are first leached out of the granules and readily interact with short-chain fatty acids.<sup>15</sup> Once an amylose–fatty acid complex is formed, the viscosity of the starch paste increases,<sup>17</sup> together with decreases in the retrogradation trend,<sup>18,19</sup> hydrophilicity,<sup>20,21</sup> and enzyme hydrolysis<sup>22</sup> of the starch material. In warp sizing, starch is the most common textile size used all the time, and traditional weavers contend that fatty lubricants, typical of which are stearic acid (SA) and sodium stearate (SS), are necessary in formulation of starch-based sizes to reduce the abrasion of warp yarns on machine parts during weaving.<sup>23</sup> Differences in the tensile, friction, and hygroscopic properties of a starch material before and after the formation of an amylose–lipid complex are expected, and the starch material is important as a sizing agent, although few studies<sup>21</sup> can be found with respect to these. The purpose of this study was to examine the effects of forming the starch–fatty complexes on the sizing properties of starch after the lubricants added.

## EXPERIMENTAL

### Materials

Native cornstarch was obtained from Guowei Starch Co., Ltd. (Xi'an, China) and was used as supplied. The moisture content of the starch was 12.7% (w/w); we gravimetrically determined this by heating the samples at 130°C for 1 h, and the amylose content in the starch granule was 24.5%, as determined by a microamount method with a spectrophotometer.<sup>24</sup> SA, SS, potassium iodide, and iodine were all analytical grade and were from Kelong Chemical Reagent Co., Ltd. (Chengdu, China). Amylose and amylopectin were purchased from Fluka Biochemika (Buchs, Switzerland). Distilled water was used in all of the experiments.

### Preparation of the pastes for the cornstarch inclusion complexes

The cornstarch of 15 g was dispersed in 485 mL of water in a three-necked bottle in a thermostatic

water bath. SA and SS were added at 1.0, 3.0, and 5.0 % w/w concentrations (relative to starch on a dry basis). The mixture was kept stirring at 360 rpm for 5 min, then was heated to 95°C, and held for 90 min under stirring to get the starch complex paste.

### Complexing indices (CIs) of the samples

With the formation of amylose–lipid complexes, the iodine-bonding capacity decreased relative to the amount of amylose occupied by the lipid.<sup>17,19</sup> The CI of a starch–lipid mixture, to represent the complexing degree, was measured by a spectrophotometric method<sup>17,19</sup> as follows. The prepared fresh complexing starch paste of 10.0 g was mixed with 23 mL of distilled water in a 50-mL capped tube. After it was shaken for 15 min, the resulting suspension of 100  $\mu$ L was taken out with a syringe and mixed with 15 mL of distilled water; this was followed by the addition of 0.17 mL of an iodine solution (2.0% KI and 0.2% I<sub>2</sub> in distilled water). The absorbance of the samples at 690 nm ( $A_s$ ) was measured with a spectrophotometer (model 721, Shanghai Instrument Co., Ltd., Shanghai, China). The absorbance of the starch paste without the addition of lipids was used as a control ( $A_0$ ). To avoid starch retrogradation, the tests were performed within 60 min. CI was calculated from the following equation:

$$\text{CI}(\%) = (A_0 - A_s) \times 100/A_0 \quad (1)$$

### Surface tension measurements

A Sigma 703 digital tensiometer (KSV Instrument, Ltd., Helsinki, Finland) was used to measure the surface tensions of 2.0 wt % starch pastes containing various concentrations of SA or SS. Each of the complex pastes in volume of 100 mL at 72.0  $\pm$  0.1°C to avoid the retrogradation of amylose was slowly poured into a glass container with a diameter of 80 mm in a thermostatic water bath, and the surface tension was measured immediately after pouring to reduce the effect of the paste skinning.

### Film formation of the starch pastes

Each of the cooked pastes in 80 mL of volume was spread out with a syringe onto a 210  $\times$  150 mm<sup>2</sup> glass dish that was paved with a polyester film of the same size and rested on a leveled surface in ambient conditions for drying. These films were used for the measurement of water vapor sorption (WVS), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

The cast films of the cornstarch inclusion complexes were too brittle to test the tensile and friction

properties; therefore, we developed two sample preparation techniques: paper sizing for tensile testing and paper coating for friction coefficient measurement.

### Paper sizing and tensile tests

A common crepe paper made of 100% wood pulp has a low strength and good liquid absorption. When the crepe paper is sized with starch paste and dried, the tensile properties mainly reflect the cohesion between starch molecules and the adhesion of starch to cellulose fiber in the sized paper. The process of the paper-sizing method includes two steps, as follows.

A piece of common crepe paper, with a size of  $150 \times 250 \text{ mm}^2$ , was clamped at one end and padded with a plastic net gauze that was slightly larger in dimensions than the crepe paper; then, the paper and the gauze pad were put into a sink plainly in distilled water for 5 min to allow the paper to soak and to loosen its internal stress. The crepe paper without any folds on the plastic net was taken away from water carefully and was hung with clips and air-dried for paper sizing.

A freshly cooked paste of 500 mL with a 3 wt % concentration of the starch–lipid mixture was put into a flat-bottom slot, and the temperature was kept at  $95^\circ\text{C}$ ; then, the pretreated paper padded with the plastic net gauze was immersed plainly into the paste and held for 5 min. After that, the crepe paper on the plastic net was taken out and hung to be air-dried; this was followed by baking in an oven at  $100^\circ\text{C}$  for 2 min.

The sized paper was separated from the plastic net carefully, cut into strips ( $10 \times 200 \text{ mm}^2$ ), and conditioned in a desiccator with a controlled relative humidity (RH) of 68% (over a saturated solution of  $\text{CuCl}_2$ ) at room temperature for 3 days before testing. The exact thickness of the paper was measured with a centesimal thickness tester (CH-10-AT, Shanghai Liuling Instrument Co., Ltd., Shanghai, China). For every sample, 10 thickness data were recorded, and their average was taken. The tensile strength (TS) and elongation at break [ $E$  (%)] for the sized papers were determined with a tensile tester (YG061, Laizhou Electron Instrument Co., Ltd., Laizhou, China) with a clamping distance of 100 mm and a stretching speed of 100 mm/min. For each set of data, 10 samples were tested, and the average values with the standard deviation were calculated.

### Paper coating and friction coefficient measurements

The friction coefficient of a material depends on the physicochemical structure and conditions of the sur-

face.<sup>25</sup> To make an acceptable surface of the starch–lipid film for friction coefficient measurement, the following paper-coating proceeded. The starch–lipid complex paste with a solid content of 3 wt % was cooked under preparation conditions of the starch inclusion complex. An adequate amount of the paste was poured onto a Kraft paperboard with a smooth surface. A threaded bar spreader (QTS-90, Tianjin Jingke Material Test Instrument Co., Ltd., Tianjin, China) was used to control the thickness of the paste layer to about 0.9 mm on the paper surface. The coated paper was air-dried and cut into a rectangular shape of  $110 \times 210 \text{ mm}^2$  for friction coefficient measurement.

The friction coefficients of both the static and the dynamic coated paper samples ( $\mu_s$  and  $\mu_d$ , respectively) were determined with a friction coefficient tester (MXZ-1, Jinan Sida Testing Technology Co., Ltd., Jinan, China). The weight of the aluminum slider onto the paper was set to 200 g with a friction area of  $63 \times 63 \text{ mm}^2$ , and the movement speed of the slider was 100 mm/min. Two data sets were obtained for the coating/metal friction pair and the intercoating friction pair, where the surface of the aluminum slider was covered with the coated paper. Ten samples were used for each data set, and the average values with the standard deviation were calculated.

### WVS

The cast films were equilibrated at room temperature for 1 week at various RHs fixed by different saturated salt solutions in corresponding desiccators. The salts used were LiCl (11% RH),  $\text{MgCl}_2$  (33% RH),  $\text{K}_2\text{CO}_3$  (44% RH),  $\text{CuCl}_2$  (68% RH), NaCl (75% RH), and  $(\text{NH}_4)_2\text{SO}_4$  (80% RH).<sup>26</sup> After equilibration, the precise weight of the samples ( $W_1$ ) was obtained. Then, the samples were dried at  $100^\circ\text{C}$  for 4 h; the weight of these was taken as  $W_2$ . The percentage of water vapor absorption was calculated as  $[(W_1 - W_2)/W_2] \times 100\%$ . Each measurement was repeated three times.

### XRD

The cast films were equilibrated at room temperature and 68% RH for 3 days before analysis. The film sample was deposited in an aluminum sample holder about 1 mm thick, and an XRD pattern was obtained with an X-ray diffractometer (D/maxIII-A, Rigaku Co., Tokyo, Japan) with Cu  $K\alpha$  radiation (wavelength = 0.15405 nm) at a voltage of 40 kV and an electric current of 35 mA. Data were collected over the  $2\theta$  range from 5 to  $50^\circ$  with a scanning speed of  $0.03^\circ/\text{s}$  and a step size of  $0.02^\circ$ . Each sample was scanned twice to average.

**TABLE I**  
**CI Values of the Starch-Lipid Complexes with Various Contents of Lipids**

Lipid content (%)	CI value (%)	
	SA	SS
1	19.4 ± 0.7	20.2 ± 0.7
3	22.6 ± 0.9	23.8 ± 0.7
4	24.1 ± 0.8	25.5 ± 0.9
5	25.2 ± 0.9	25.5 ± 0.8
8	23.5 ± 0.7	25.5 ± 0.8

$$CI_0 = 0.453 \pm 0.7\%$$

### SEM observation

The cast films were sputtered with gold and then observed with a scanning electron microscope (Inspect F., FEI Co., Hillsboro, OR).

## RESULTS AND DISCUSSION

### CI

The capacity of amylose to bind iodine will be reduced if the helix is occupied by a lipid,<sup>8</sup> and not all the lipid molecules can participate in the complexing reaction, which depends on the size and physicochemical properties of the lipid.<sup>27</sup> According to the definition of CI,<sup>19</sup> the CI value reflects the ability of amylose in starch to form an inclusion complex with a ligand. So, a larger CI value means a lower  $A_s$  and that more inclusion complexes have formed between amylose and the ligand.

The CI value of starch without the addition of any lipid ( $CI_0$ ) was equal to 0.453%; this was caused by native lipids in cornstarch.<sup>1,28</sup> As shown in Table I, the CI value gradually increased with increasing SA or SS and then reached a maximum. Amylose helices occupied by lipids had a reduced capacity to bind iodine and gave a lower absorbance than the starch alone. For an SA content of 5%, the CI reached a maximum value of 25.2% and then decreased as SA was added further. Perhaps it was because of the poor water solubility of SA. Above a certain concentration, therefore, it had a tendency to self-associate rather than form complexes with amylose helices.<sup>18</sup> Although in the case of SS, CI increased to a maximum of 25.5% at 4% SS. When the maximum CI values of the two lipids were compared, the inclusion complex of SS was formed readily with amylose because of the available monomer in water for its relatively higher water solubility.<sup>17,28</sup>

### Surface tension

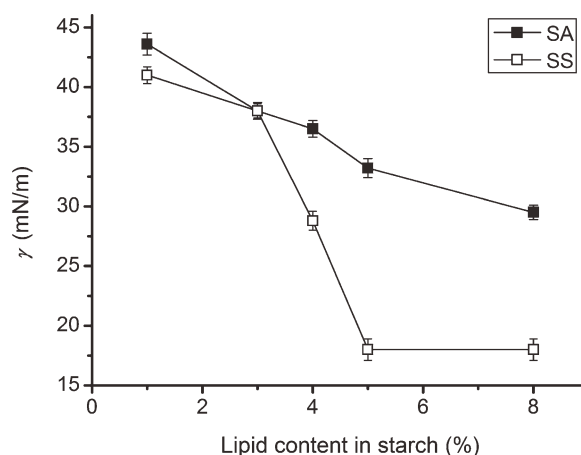
The surface tension ( $\gamma$ ) of the aqueous complex systems decreased with the addition of lipids, as shown in Figure 1. The phenomenon suggested that in the

aqueous system, part of the lipid molecules were adsorbed at the air/water interface. The difference in the surface activity between the two starch-lipid complexes was obvious, as shown in Figure 1. As the SS content reached 3% on the basis of starch, the surface tension of the complex system went through a rapid decline until 5% SS was reached, above which no changes of the surface tension appeared. This surface tension-concentration profile showed a typical surfactant characteristic, whereas in the case of SA, the surface tension of the paste decreased gradually with increasing SA content. The lower surface activity was likely attributed to the weaker polarity of the carboxyl groups in SA than that in the ionized carboxylic acid in SS. In the course of the formation of the amylose-SA inclusion complex, the self-aggregation of the SA molecules occurred because of its lower solubility in water.

At the test temperature of 72°C, the surface tension of the 2% starch paste without lipids was 55.0 mN/m. The addition of lipids, especially for SS, lowered the surface tension of the paste greatly; this facilitated wettability and the penetration of the starch-sizing agent to yarns. In this sense, SS excelled SA as a textile-sizing auxiliary.

### WVS

WVS or the hygroscopicity of a polymer depends on its hydrophilic groups in the molecule and the accessibility of the groups. A hydroxyl group as a characteristic functional group of starch is sensitive to water vapor. Table II shows the effect of the lipids content in starch on WVS of the complex films. At 11% RH, WVS of the complex films was always higher than that of the film containing starch only, whereas at a higher RH of 68%, the WVS value of the complex films was always less than that of the film containing starch only. One of reasons for this



**Figure 1** Surface tensions of 2% starch pastes with various contents of lipids.

**TABLE II**  
WVS of the Starch–Lipid Complexes with Various Contents of Lipids

Lipid content (%)	SA		SS	
	11% RH	68% RH	11% RH	68% RH
0	9.84 ± 0.54	19.28 ± 0.65	9.84 ± 0.54	19.28 ± 0.65
1	13.33 ± 0.69	16.71 ± 0.77	15.63 ± 0.72	16.50 ± 0.70
3	13.49 ± 0.79	12.37 ± 0.75	11.43 ± 0.66	19.15 ± 0.68
5	10.54 ± 0.71	13.05 ± 0.73	12.98 ± 0.73	13.95 ± 0.72

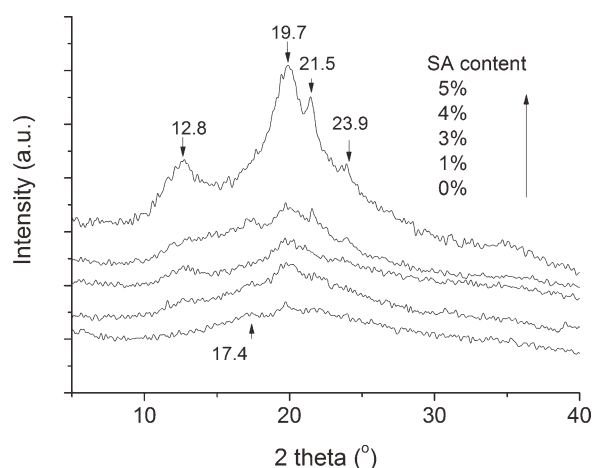
phenomenon might have been the formation of the V-type crystal (single helix) of amylose in the presence of lipids, with a conformation of a hydrophobic cavity to accommodate the lipid stretching inside and hydroxyl groups of amylose located on the outer surface of the helix.<sup>3,4</sup> Films formed from starch pastes without lipids generally show a B-type crystalline structure<sup>29</sup> composed of double-strand helices of two parallel-strand (6/1) single helices and a total of 36 water molecules contained in a unit cell.<sup>30</sup> At a lower RH, a V-amylose with exposed hydroxyl groups could absorb more water molecules than a B-type crystal, whereas at a higher RH, a more compact structure of a V-amylose inclusion complex formed,<sup>31</sup> in which hydroxyl groups were embedded in the V-amylose crystal and were less sensitive to environmental RH. On the other hand, in addition to the formation of the inclusion complex, the hydrophobic lipids could also associate by self-aggregation in the starch matrix and on the surface of the starch film. The hydrophobic lipid layer on the surface or congeries in the matrix hindered the exchange of water into or out the film; this made the complex films less sensitive to environmental moisture; that is, under different RH conditions, the starch–lipid complex film presented average WVSs. This was in favor of warp sizing because of the decreased effect of environmental moisture on weaving.<sup>32</sup>

To understand the mechanism behind the properties mentioned previously, characterization of the crystal structure was needed.

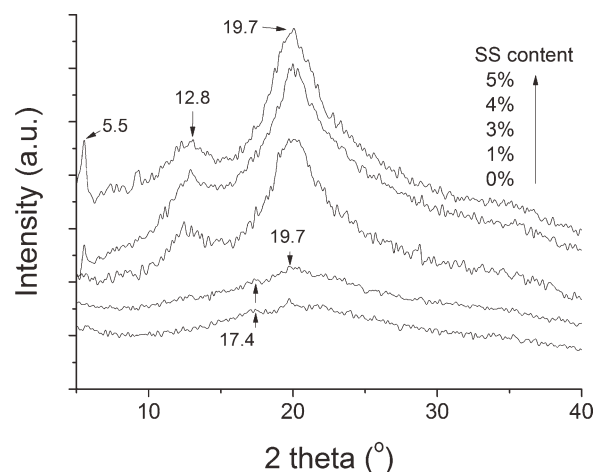
### XRD of the starch–lipid complexes

The crystal structure of the cornstarch without lipids changed from A-type in granules to a B-type crystal of double helix after pasting.<sup>29,33</sup> Figure 2 shows XRD patterns of the films of cornstarch–SA complexes. The A-type crystal of granules was disintegrated, and there existed a weak peak at  $2\theta = 17.4^\circ$  belonging to a B-type crystal<sup>34</sup> and a peak at  $19.7^\circ$  of V-type crystal.<sup>28</sup> For the control sample without lipids added, a V-type pattern at a peak of  $2\theta = 19.7^\circ$  might have resulted from naturally occurring lipid material.<sup>28</sup> With increasing amount of SA added, typical peaks of the V-type crystal<sup>28</sup> at  $2\theta = 12.8, 19.7, 21.5,$  and  $23.9^\circ$  became more evident. In Figure 3, the shape and intensity of the V-type peaks at 4% SS content were similar to that at 5% SS. This result was consistent with the previous CI analysis.

Further analyses of the total crystallinity (TC), relative crystallinity (RC), and crystallite size (CS) of the films for both the starch–SA and starch–SS were calculated by MDI Jade 5.0 software (Materials Data, Inc., Livermore, California) from the data of Figures 2 and 3, and the results are presented in Table III. It was found that the TC value of the complex films increased



**Figure 2** XRD patterns of the starch complex films with various contents of SA.



**Figure 3** XRD patterns of the starch complex films with various contents of SS.

**TABLE III**  
**TC, RC, and CS Values of the Films for Cornstarch, Starch-SA, and Starch-SS Inclusion Complexes**

Dosage (%)			RC (%)		CS (Å)	
SA	SS	TC (%)	2θ		2θ	
			17.4°	19.7°	17.4°	19.7°
—	—	0.41	0.28	0.18	122.12	106.38
1	—	3.16	0.27	2.12	76.31	55.71
3	—	5.79	0.21	2.56	54.95	68.20
4	—	6.69	0.26	3.83	61.72	70.49
5	—	13.88	0.20	7.45	52.36	98.78
—	1	0.42	0.23	0.25	78.86	55.01
—	3	12.35	0.22	6.23	51.25	80.20
—	4	13.74	0.22	7.31	52.71	94.89
—	5	13.95	0.23	7.56	52.85	96.38

gradually with the addition of SA and rapidly with the addition of SS in the lipid content range from 1 to 4%; this was mainly attributed to the increase of RC at  $2\theta = 19.7^\circ$ . On the other hand, as any one of the lipids was added, CS at  $2\theta = 17.4^\circ$  for the B-type crystal in the films decreased. This suggested that the lipids could restrain B-type crystal growth in the cornstarch and reduce CS of the B-type crystal.

#### Friction coefficient of the starch-lipid films

Table IV shows the effect of the addition of lipids on the friction coefficients of starch films. The largest friction coefficient was observed for the film of starch only; when either of the lipids was added, the friction coefficients of both  $\mu_s$  and  $\mu_d$ , whether for friction pairs of intercoating or for coating/metal, significantly decreased and reached the minimum at 1% lipids. This could have resulted from two factors. The first could have been that both lipids increased the smoothness of the surfaces of complex film visibly. The second was that apart from an inclusion complex with starch, some noncomplex lipid molecules migrated from the starch matrix to the film surface as boundary lubricants. The migration of lipid monomer occurred because of its hydrophobic nature in the aqueous medium.<sup>25</sup> The lower friction coefficients of the starch film would be in favor of wear-resistance properties for sized yarns because the yarns coated by the size film could work under more friction from moving parts of the weaving machine and other yarns during weaving.

#### SEM observation

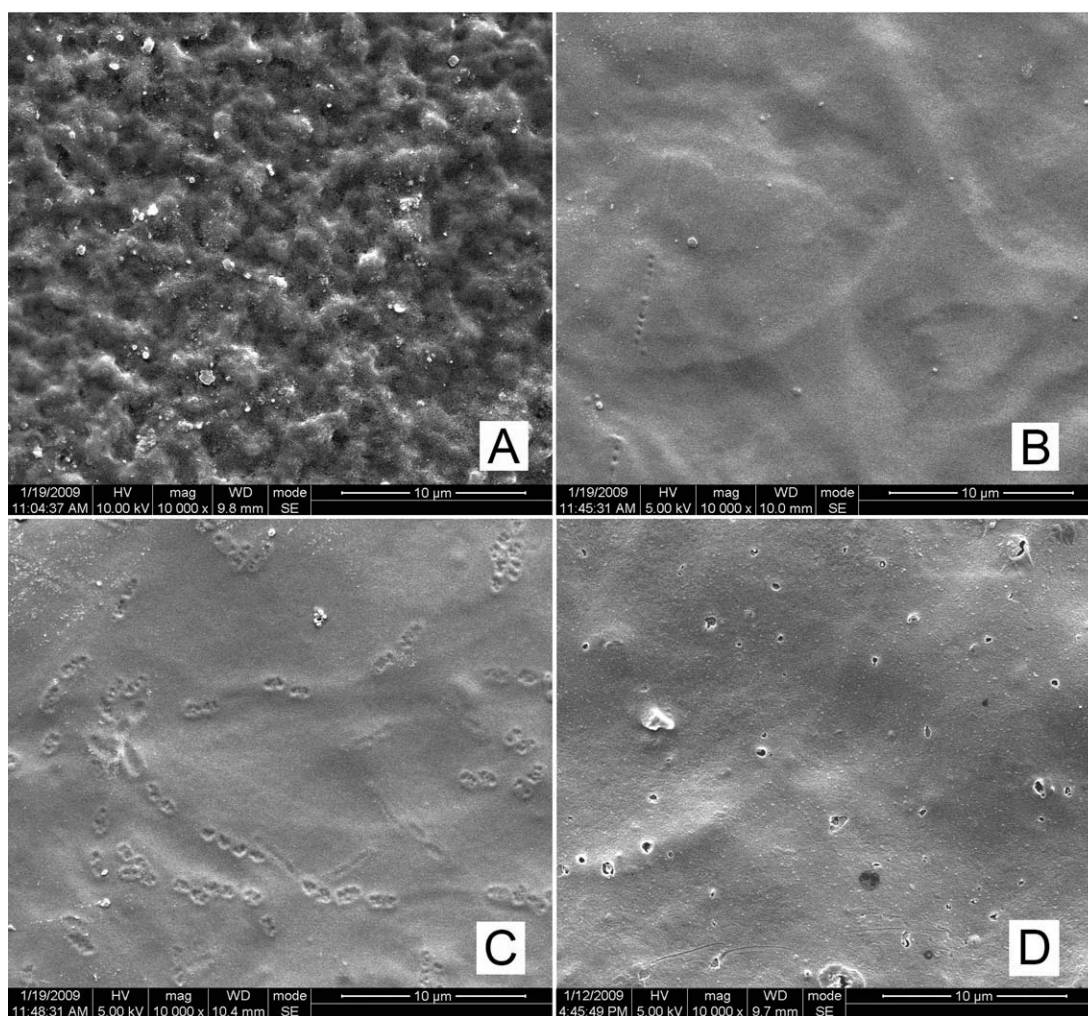
From the friction coefficient test, we knew that the friction coefficients of the starch film were lowered greatly by the addition of lipids; this could be interpreted intuitively by analysis of the surface structure, as shown by SEM photos in Figures 4 and 5.

Figure 4(A) shows the SEM photo of the film of starch only. We observed an irregular ridged structure on the film surface, which was presumably due to the retrogradation of amylose and amylopectin in the course of slow film formation at room temperature as a result of a B-type crystal formed gradually.<sup>35</sup> Figure 4(B–D) shows SEM photos of the complex films by additions of SA of 1, 3, and 5%, respectively. Obviously, the surface of the complex films became more smooth, relatively even, and basically defect-free; this indicated that the formation of the V-type inclusion complexes had an ability to level the starch surface because of reduced crystallite dimensions, as Table III shows, and then to lower the friction coefficients (Table IV). With increasing SA over 1%, however, there were pits (for 3% SA) and holes (for 5% SA) that made the film surface uneven. The pits and holes were presumably from traces after the volatilization of SA aggregates under high vacuum during SEM observation.

Figure 5 shows the SEM photos of the starch films with or without SS. Just like the case of SA, the addition of SS made the surface of the complex film

**TABLE IV**  
**Friction Coefficients of Complex Films with Various Contents of Lipids**

Friction pair		Starch only	SA			SS		
			1%	3%	5%	1%	3%	5%
Intercoating	$\mu_s$	$0.23 \pm 0.06$	$0.17 \pm 0.08$	$0.18 \pm 0.06$	$0.19 \pm 0.06$	$0.17 \pm 0.08$	$0.18 \pm 0.07$	$0.19 \pm 0.08$
	$\mu_d$	$0.20 \pm 0.07$	$0.16 \pm 0.07$	$0.16 \pm 0.07$	$0.18 \pm 0.07$	$0.15 \pm 0.08$	$0.16 \pm 0.07$	$0.17 \pm 0.07$
Coating/metal	$\mu_s$	$0.34 \pm 0.08$	$0.20 \pm 0.08$	$0.20 \pm 0.07$	$0.22 \pm 0.07$	$0.19 \pm 0.08$	$0.20 \pm 0.07$	$0.23 \pm 0.08$
	$\mu_d$	$0.29 \pm 0.08$	$0.18 \pm 0.08$	$0.18 \pm 0.08$	$0.19 \pm 0.07$	$0.17 \pm 0.07$	$0.18 \pm 0.07$	$0.20 \pm 0.08$



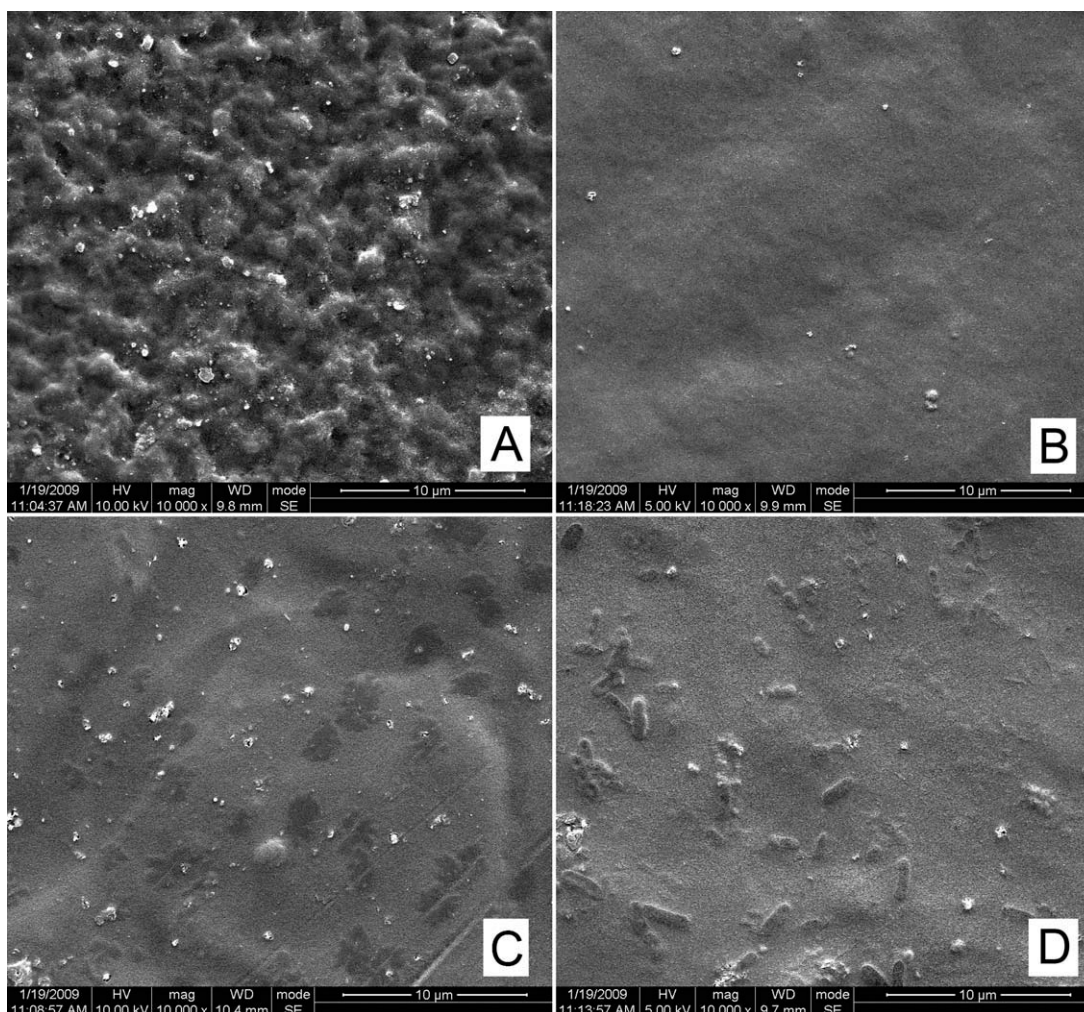
**Figure 4** SEM images of the (A) cast starch film and its complex films with SA of (B) 1, (C) 3, and (D) 5% based on dry starch.

smoother; this may have arisen from the V-type crystals of amylose–SS complexes, which could restrain the B-type crystallization of starch, as reflected in Table III. With further increases in the amount of SS, some disorderly accumulation of oily matter for 3% SS and rod-shaped objects for 5% SS appeared on the film surfaces. The mechanism might have been that in addition to complexing with amylose and, according to surface tension curves in Figure 1 and CI values in Table I, SS molecules tended to adsorb to the surface of the paste as Tang and Copeland<sup>19</sup> observed in a system of starch–fatty acids and to self-associate on the film surface when dried. Because of the ionization of SS, its aggregate or crystallite was not as easy to volatilize as SA did under vacuum conditions.

On the basis of the fact that the surface roughness was highly consistent with the friction coefficients in Table IV, we confirmed that a small amount of lipids, 1 wt % SA or SS here, was needed in the starch-based warp-sizing agent.

### Tensile properties

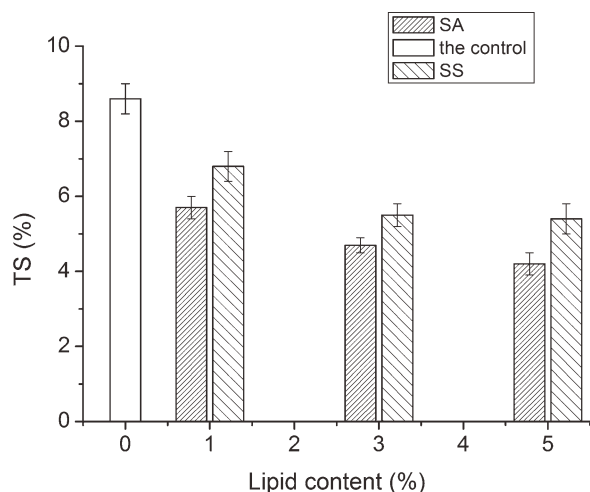
From the previous discussion, the addition of lipids changed the crystal structure and the surface texture of the starch films. As a result, the tensile properties of the films were then altered, as shown in Figures 6 and 7. The pretreated crepe paper had a TS of  $0.5 \pm 0.2$  MPa and an  $E$  of  $3.24 \pm 0.42\%$ . Once sized with the starch, the paper gained a TS of  $8.6 \pm 0.4$  MPa and an  $E$  of  $11.75 \pm 0.59\%$ . As SA was added to the starch, however, the TSs of the complex films dropped immediately and gradually decreased further with increasing SA. The variation trend of TS was relative to the CI values in Table I and the RCs at  $2\theta = 19.7^\circ$  in Table III; this indicated that the V-type crystal was a main effect factor on the TS. On the other hand, the  $E$  of complex films reached the maximum at a 1% content of SA, higher than that of starch only, and then decreased with SA addition. Therefore, an SA content in excess of 1% in the starch matrix was destructive to both the TS and  $E$  of the starch film.



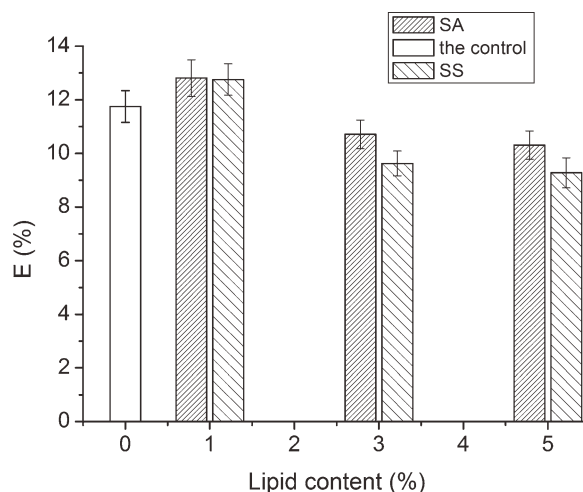
**Figure 5** SEM images of the (A) cast starch film and its complex films with SS of (B) 1, (C) 3, and (D) 5% based on dry starch.

When SS was added, the variation trend of the tensile properties of complex films were similar with those with the addition of SA. The differences were

embodied as a smaller loss of TS and a larger loss of *E* for the starch–SS system than for the starch–SA system. This was likely due to some micellar



**Figure 6** TS values of films for cornstarch, starch–SA, and starch–SS inclusion complexes



**Figure 7** *E* values of films for cornstarch, starch–SA, and starch–SS inclusion complexes



structures of SS in the starch matrix leading to a more compact film in comparison with the starch-SA material as a result of the nonmicellar structure of SA in the starch film, as Figure 1 indicates.

For starch films of the two starch-lipids complexes, *E* reached a maximum at 1% lipids. The reason could have been that the addition of a small amount of lipids into the starch would have prevented the formation of an amylose double helix and inhibited the B-type crystal. The aggregation structure of the starch material was loosened in the case of the lesser crystallinity of starch. With increasing lipid addition, the amount of V-type crystals increased gradually for the starch-SA system and greatly for the starch-SS system, as shown in Figures 2 and 3 and Table III. The V-type crystal contributed directly to TC so that *E* decreased for the starch-SA system and decreased more for the starch-SS system.

According to the data in Figures 6 and 7, once either SA or SS was complexed with the starch, the TS decreased and *E* first increased and then decreased with increasing lipid content. In the case of 1% lipids added, better tensile properties of the starch-lipid complexes were obtained with less loss of strength and enhanced *E*.

## CONCLUSIONS

Cornstarch formed inclusion complexes with SA and SS, respectively, during the course of pasting. When SA reached 5 wt % or SS approached 4 wt % on the basis of starch, respectively, the inclusion complexing seemed to be saturated. The SS molecules not included in amylose tended to adsorb to the paste surface or form micelles in the starch paste; this reduced the surface tension of the paste greatly, whereas the noncomplex SA self-associated in the starch paste in the form of nonmicelle, which contributed less to the surface tension. The V-type crystallinity increased in the starch films with increasing amount of SA or SS to increase TC. The B-type CS was greatly decreased upon addition of the lipids to the starch paste, and we also observed by SEM that the film surface became smoother. The results of the friction coefficient indicated a close relationship between the friction coefficient and the surface roughness of the starch film. Amylose-lipid inclusion complex made the WVS of the starch film less sensitive to the various environmental RHs. In other words, WVS of the film containing the inclusion complex was higher at a lower environmental humidity and lower at a higher environmental humidity in comparison with the starch film without lipids. The TS of the starch complex decreased with increasing amount of SA or SS in the starch, whereas *E* reached a maximum at a lipid loading of

1% and then decreased with further loading. In short, the tensile properties of the starch film were greatly affected by the formation of the V-type crystal.

On the basis of the results that our study revealed, the addition of either SA or SS to the starch-based material was in favor of such properties as a lower surface tension of the paste, reduced friction coefficient of the starch film, and less sensitivity to various RH conditions in a sense of moisture adsorption of the film. However, the addition of lipids, especially of more than 1% in amount, reduced the tensile properties of the starch-based film.

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